

Film-Forming Polymers Containing in the Main-Chain Dibenzo Crown Ethers with Aliphatic (C₁₀–C₁₆), Aliphatic–Aromatic, or Oxyindole Spacers

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ABSTRACT: Novel, linear, soluble, high-molecular-weight, film-forming polymers and copolymers in which main-chain crown ether units alternate with aliphatic (C₁₀–C₁₆) units have been obtained for the first time from aromatic electrophilic substitution reactions of crown ethers by aliphatic dicarboxylic acids followed by reduction of the carbonyl groups. The crown ether unit is dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8, or dibenzo-30-crown-10; the aliphatic spacer is derived from a dicarboxylic acid (sebacic, 1,12-dodecanedicarboxylic, hexadecanedioic or 1,4-phenylenediacetic acids). The reactions were performed at 35 °C in a mixture of methanesulfonic acid (MSA) with phosphorus pentoxide, 12:1 (w/w), (Eaton's reagent). The carbonyl groups in the polyketones obtained were completely reduced to methylene linkages by treatment at room temperature with triethylsilane in a mixture of trifluoroacetic acid and dichloromethane. Polymers containing in the main chain crown ethers alternating with oxyindole fragments were prepared by one-pot condensation of crown ethers with isatin in a medium of Eaton's reagent. A possible reaction mechanism is suggested. According to IR and NMR analyses, the polyacylation reactions lead to the formation of isomeric (syn/anti-substituted) crown ether units in the main chain. The polymers obtained were soluble in the common organic solvents, and flexible transparent films could be cast from the solutions. DSC and X-ray studies of the polymers with "symmetrical" crown ethers reveal the presence of the endotherms corresponding to the supramolecular assemblies.

1. Introduction

Cyclic polyethers (crown ethers) are one of the most interesting topics in chemistry. Discovered and first described (in a very impressive by even modern criteria series of three papers) by A. Luttringhaus in 1937,¹ cyclic polyethers were synthesized in 1960 by C. J. Pedersen,² who recognized the remarkable ability of crown ethers to complex with a variety of cations. In more recent years, such macrocycles have also become important starting materials for the building of supramolecular assemblies, sensors for ions, and molecular scaffolds, which thereby stimulated an additional interest within

the field. Numerous books and reviews on crown ethers have been published, many recently.³

Obviously, incorporation of crown ethers into polymer chains offers additional advantages for their application, such as ease of handling, facility of recovery, and modification of their complexation properties. Besides, crown-containing polymers are of major interest as new materials. This is why there has been a significant progress in the area of crown-containing polymers over the last two decades.⁴

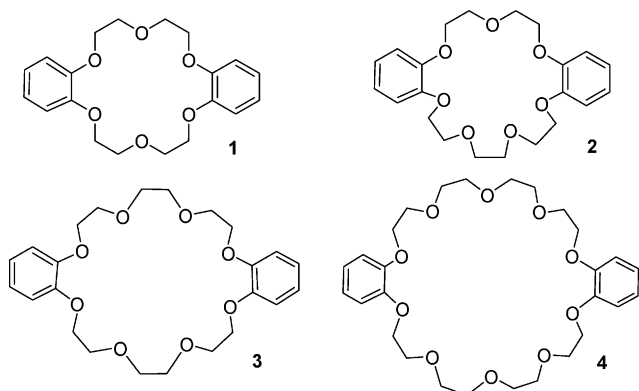
There are three principal methods by which crown ethers can be incorporated into polymer matrixes. The first is direct polymerization of the crown ether through a step-growth mechanism; the second is polymerization through a chain-

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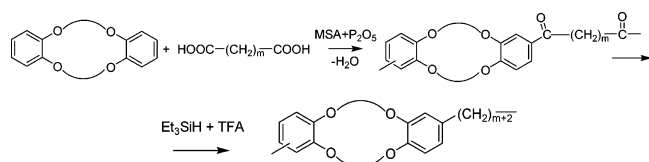
growth mechanism; and the third is postfunctionalization wherein a crown ether is covalently bound to a preformed polymer backbone. Clearly, simple, reliable syntheses of crown-containing polymers combined with the minimum number of reaction steps would be of great importance.

One of the most promising approaches for one-step preparation of crown-containing polymers is Friedel–Crafts chemistry. Ueda reported⁵ successful condensations of dibenzo-18-crown-6 ether with aliphatic diacids in an Eaton's reagent medium (phosphorus pentoxide in methanesulfonic acid, 1:10, w/w). However, structural characterization of the polyketones was very limited, and no morphology data were presented.

In this paper, we describe synthesis and characterization of crown-containing polymers obtained by acylation of dibenzo-18-crown-6 (**1**), dibenzo-21-crown-7 (**2**), dibenzo-24-crown-8 (**3**), and dibenzo-30-crown-10 (**4**) ethers:

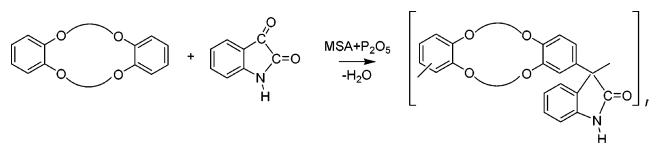


with sebacic (**a**), 1,12-dodecanedicarboxylic (**b**), 1,16-hexadecanedioic (**c**), and 1,4-phenylenediacetic acids (**d**) and their mixtures, followed by metal-free, quantitative reduction of the resulting carbonyl groups, which leads to the formation of fully aliphatic spacers between crown ether units according to the following general scheme:



The reduced polymers are the first to comprise crown ether systems (including macrocyclic rings with up to 30 atoms) connected by simple, aliphatic hydrocarbon linkages. As shown below, this novel type of structure leads to an unexpectedly high degree of order in the solid state, despite clear NMR evidence for a random sequence of syn- and anti-substituted dibenzo-crown residues within the polymer chain.

Polymers containing in the main chain crown ethers alternating with oxyindole fragments were prepared by condensation of crown ethers with isatin (**e**):



The structures of the polymers obtained and their general properties are reported.

2. Experimental Section

2.1. Materials. Triethylsilane, dibenzo-18-crown-6, dibenzo-21-crown-7, dibenzo-24-crown-8, and dibenzo-30-crown-10 ethers

were obtained from Aldrich and used as received. Sebacic, perfluorosebacic, 1,12-dodecanedicarboxylic, 1,16-hexadecanedioic, and 1,4-phenylenediacetic acids were obtained from Aldrich and purified by reprecipitation through their potassium salts. Isatin was obtained from Aldrich and recrystallized from ethanol. Trifluoroacetic, trifluoromethanesulfonic, and methanesulfonic acids were obtained from Fluorochem Ltd. and distilled prior to use.

2.2. Characterization. The inherent viscosities of 0.2% polymer solutions in 1,1,2,2-tetrachloroethane (TCE) were measured at 25 °C by using an Ubbelohde viscometer. The ¹H and ¹³C NMR spectra were recorded using a Bruker Avance 400 spectrometer. Differential scanning calorimetry (DSC) measurements were performed at 20 °C min⁻¹ on a DSC 2910 from TA Instruments. Molecular weights of polymers **3a** and **4b** were determined by gel permeation chromatography (GPC) using a Waters gel permeation system (Waters 2695 ALLIANCE) coupled with a refraction detector Waters 2140. The chromatography system was equipped with Waters styragel columns HSGel HR MB-L (*M_w*: 5·10²–7·10⁵) and HSPgel HR MB-B (*M_w*: 1·10³–4·10⁶). The measurements were made at 35 °C with THF as the solvent at a flow rate of 0.5 mL/min. Molecular weights of the rest of the polymers were determined with a chromatograph equipped with a pump (Varian 9002), column TSK-gel type G4000H connected with refractometer detector (Varian RI-4) and integrator (Varian 4400) coupled with GPC-Plus software. *N,N*-Dimethylformamide of HPLC grade was used as eluent at 25 °C at a flow rate of 1 mL/min. The system was calibrated with polystyrene TSK standard 5·10² to 7·10⁵ from TOSOH, Japan. Molecular weights (GPC) were calculated with a calibration plot constructed with polystyrene standards. Thermo-mechanical analysis (TMA) was conducted with a TA Instruments TMA 2940 instrument. The TMA experiments were carried out at a scan rate of 10 °C min⁻¹ using a penetration probe of 1.0 mm diameter under an applied constant load of 1N. Softening temperatures (*T_{soft}*) were taken as the onset temperature of probe displacement on the TMA traces.

2.3. Polymer Synthesis. **2.3.1. Polymer Syntheses Involving Crown Ethers and Diacids.** A typical example of polymer preparation was as follows. Eaton's reagent (4 mL) was added to a mixture of dibenzo-18-crown-6 ether (0.451 g, 1.25 mmol) and sebacic acid (0.253 g, 1.25 mmol). The reaction mixture was stirred for 7 h at 35 °C and poured into water. The slightly yellow fiber formed was filtered off, washed with water, and extracted with hot methanol and acetone. After drying, 0.673 g (98%) of white fiberlike polymer was obtained. The inherent viscosity of the 0.2% solution of the polymer (**1a**) in TCE was 0.93 dL g⁻¹.

A mixture of the polymer thus obtained (0.256 g, 0.48 mmol), TFA (2.0 mL), and dichloromethane (2.5 mL) were magnetically stirred under a nitrogen atmosphere for 20 min, during which time the polymer dissolved completely to give a deep-violet-colored solution. Triethylsilane (1 mL, 6.26 mmol) was then added dropwise over 30 s, and the mixture was stirred under nitrogen for 18 h and then poured into ethanol. The white precipitate that formed was filtered off and washed with hot methanol and acetone. Filtration and drying gave the reduced polymer (0.186 g, 77%) of viscosity 1.05 dL g⁻¹. The ¹H NMR spectrum of polymer (**1aH**) is presented in Figure 3.

2.3.2. Polymer Syntheses Involving Crown Ethers and Isatin. Isatin (0.294 g, 2.00 mmol), dibenzo-24-crown-8 (0.897 g, 2.00 mmol), trifluoroacetic acid (2.1 mL), and Eaton's reagent (3.1 mL) were stirred under dry nitrogen at room temperature for 1.5 h, and the resulting clear, viscous, red solution was then poured slowly into water (200 mL). The pale-yellow solid was filtered off, washed copiously with water, and then extracted with refluxing methanol and finally with acetone, before drying at 100 °C under vacuum. The resulting pure-white fibrous polymer **3e** (1.14 g, 98.6%) had an inherent viscosity of 0.88 dL g⁻¹ (NMP). Polymer **1e** was obtained by entirely analogous procedure.

3. Results and Discussion

3.1. Polymer Syntheses and Structures. Generally, preparation of polyketones based on dibenzo-18-crown-6 ether and

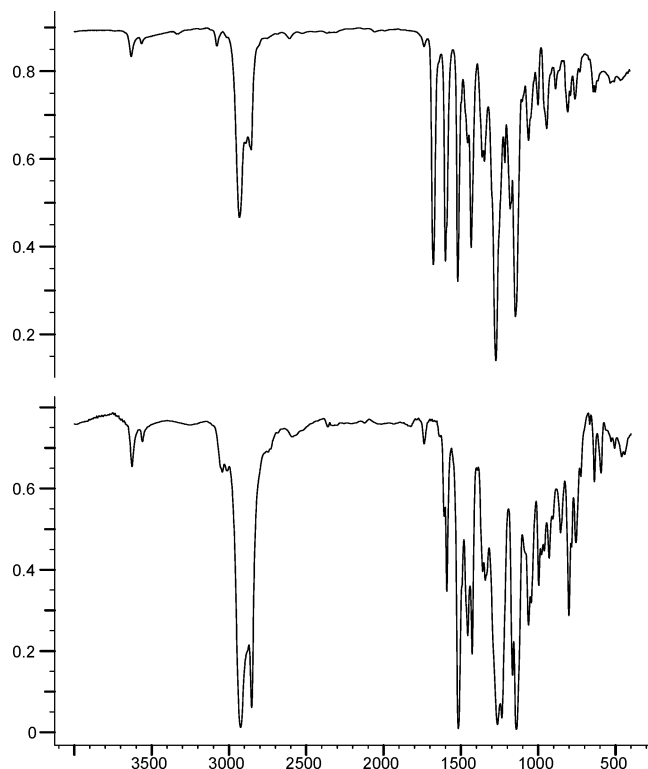


Figure 1. IR spectra of **1a** and **1aH** (films). Top: polyketone **1a** as obtained. Bottom: reduced polymer **1aH**.

aliphatic diacids has been carried out at room temperature for 24 h or even longer.⁵ By optimizing reaction conditions, we have found that syntheses at 35 °C in Eaton's reagent with a lower concentration of phosphorus pentoxide, (8%, vice 10%) result in high-molecular-weight polymers with reaction times between 7 and 9 h. Further increase of the reaction temperature, e.g., up to 40–45 °C, leads to cross-linking. All the polymer preparations proceeded in homogeneous solution. The reaction mixtures were precipitated into water after reaction completion; the polymer formed a yellow fiber which, after hot extraction with methanol and acetone, changed color to pale yellow or white. Yields of the polymers obtained were nearly quantitative.

The IR spectra of the polymer films revealed the expected presence of the band at 1670 cm⁻¹, corresponding to the carbonyl group, and a set of bands corresponding to the aromatic, aliphatic, and ethylene oxide fragments (Figure 1, top).

Additionally, the IR spectra of polymers with dibenzo-18-crown-6 ether units show two bands at 3636 and 3571 cm⁻¹. It is known that dibenzo-18-crown-6 ether can form complexes with water,⁶ therefore, we simulated the IR spectrum with a model compound, a complex of diacetoxydibenzo-18-crown-6 ether with water, using the Jaguar 5.5 suite of programs and optimizing the geometry of diacetoxydibenzo-18-crown-6 at B3LYP/6-31G* level of theory and running the frequency job at the same level of theory by using a scaling factor of 0.9614 for frequency calculations. Calculated vibrational frequencies corresponding to the antisymmetrical and symmetrical OH₂ vibrations in the complex were found to be 3658 and 3542 cm⁻¹, respectively. The structure of the model complex is presented in Figure 2.

As seen from the figure, the complex is stabilized by hydrogen bonding between crown oxygens and water hydrogens. The hydrogen bond lengths are of 2.02 and 2.30 Å, involving aliphatic and aromatic oxygens, respectively. The shorter distance for the first hydrogen bond is consistent with more basic character of aliphatic oxygen compared to aromatic one.

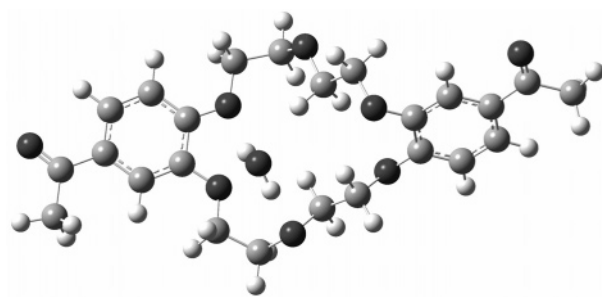
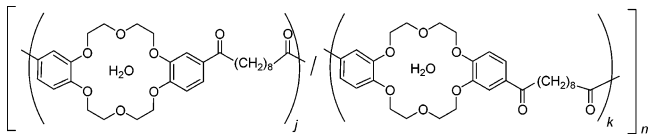


Figure 2. Calculated structure of the complex of 3,4'-diacetoxydibenzo-18-crown-6 ether with water.

The good solubility of the polymers has allowed analysis of their structures by NMR spectroscopy. The ¹H NMR spectra of the polymers (Figure 3) are well resolved and unambiguously point to meta- and para-substitution (in relation to C–O bonds) in aromatic rings.

¹³C NMR spectra of the polymers are also well resolved. Interestingly, the ¹³C NMR spectrum of polymer **1a** shows two sets of signals (approximately of equal intensity), corresponding to the carbons of aromatic nuclei. One may observe even splitting of the carbonyl signal at 199.5 ppm (Figure 4). Therefore, there are two isomeric structures (syn- and anti-substituted crown ether residues) within the polymer chains, and the chemical composition of the polymer **1a** can be represented by the following scheme:

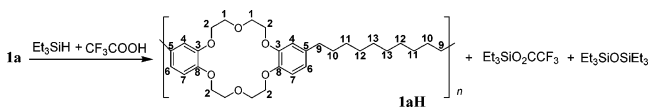


As a matter of fact, such polymer structure is also in agreement with the results of acylation of dibenzo-crown ethers, resulting in two isomer diacyl derivatives.⁷ Polymers containing dibenzo-21-crown-7 and dibenzo-24-crown-8 ether units also reveal similar splitting; however, the larger the size of the macrocycle, the smaller the splitting becomes (Figure 5).

Although the ¹³C NMR spectra of the polymers containing the largest macrocyclic residue (dibenzo-30-crown-10 ethers) do not reveal similar splitting of aromatic carbon signals, presumably as a result of the increased spatial separation of the substituted rings, there seems to be no reason that these polymers should not also contain analogous isomeric structures.

It is known that the extent of the conversion in many polymer-derivatization reactions is not very high. By taking into account the presence in the polyketones of obtained macrocycles (more exactly, their complex formation ability), application of traditional reductive methods (such as Clemmensen and Wolf–Kishner reactions or reduction in the presence of Raney nickel) is not promising. Therefore, we turned our attention to reduction of carbonyl groups to methylene groups by use of triethylsilane in trifluoroacetic acid media.⁸ Recently, the method was successfully used for the reduction of carbonyl groups in aromatic polyketones.⁹

In the present work, the reductions were carried at room temperature according to the following scheme: simply by



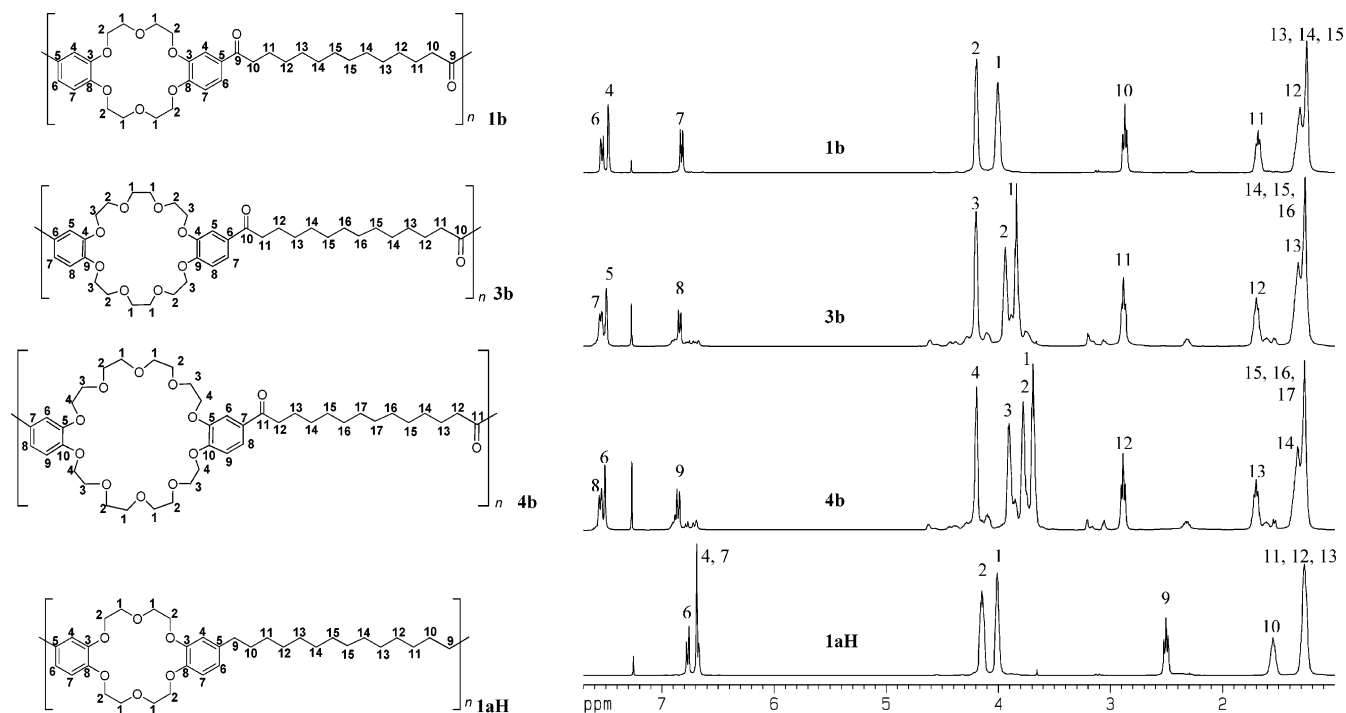


Figure 3. ^1H NMR spectra of polymers **1b**, **3b**, **4b**, and **1aH** (solutions in CDCl_3).

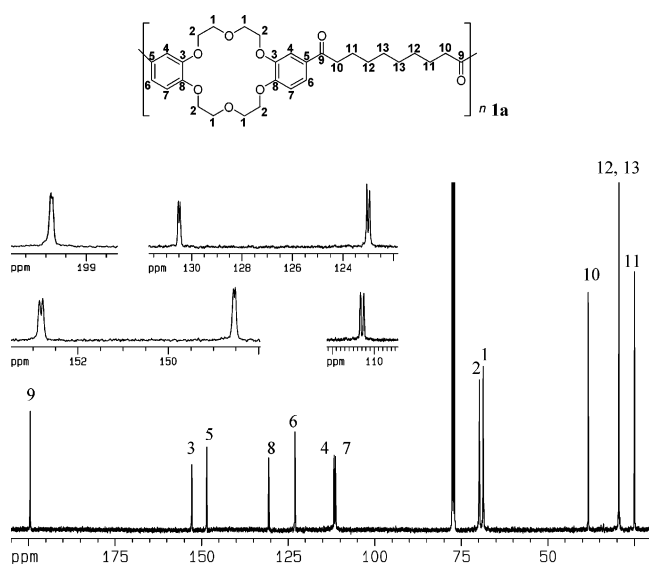


Figure 4. ^{13}C NMR spectrum of polymer **1a** (solution in CDCl_3).

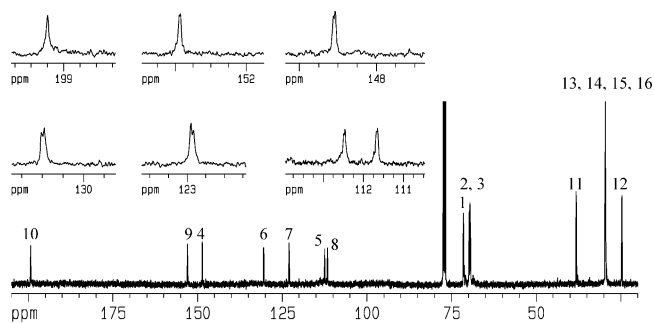


Figure 5. ^{13}C NMR spectrum of polymer **3b** (solution in CDCl_3).

dissolving a crown-containing polyketone in a mixture of methylene chloride and trifluoroacetic acid, adding triethylsilane, and stirring overnight. In all cases, the product, which remained

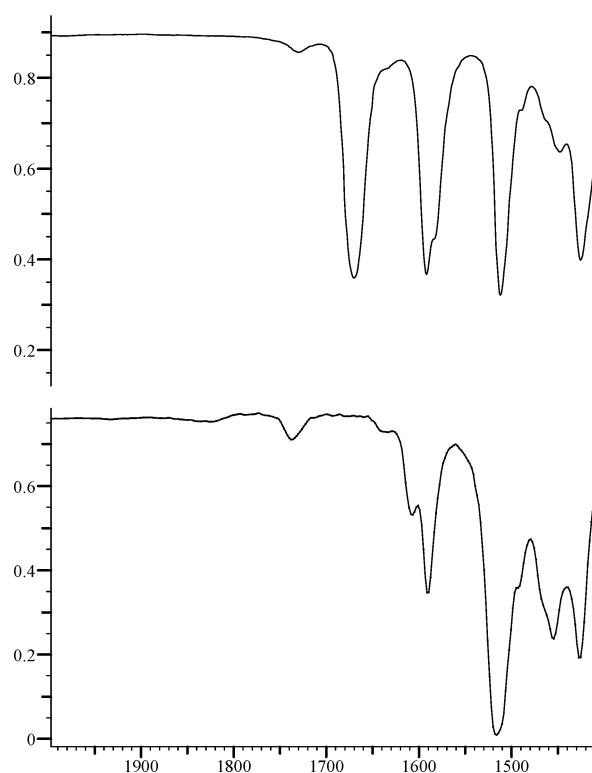


Figure 6. Expansion of the carbonyl region of the IR spectrum of polymer films **1a** (top) and **1aH** (bottom).

in solution at the end of the reaction period, was recovered by precipitation into ethanol. The progress of reduction was estimated by sampling the reaction at intervals and analyzing the product by FT-IR spectroscopy (disappearance of the carbonyl band near 1670 cm^{-1}) and by ^1H NMR spectroscopy (appearance of a new singlet near 2.5 ppm, resulting from the methylene residues, and a marked upfield shift of the lowest-field aromatic proton signals, Figure 3). When reaction was complete, the IR spectra of the reduced polymers (Figure

1, bottom and Figure 6) showed no sign of the band corresponding to carbonyl groups. By taking into account the generally high intensity of the band, it is clear that reduction is essentially quantitative. Similar treatment of the rest of the polymers with triethylsilane-produced polymers containing methylene groups instead of carbonyl ones was made.

Copolymers containing different aliphatic spacers or different macrocycles were also successfully obtained, for example, by reaction of macrocycle **1** with a mixture of diacids (**a** + **b**) and macrocycle mixture (**1** + **3**) with diacid **a**. The syntheses of the copolymers proceeded similarly to the syntheses of homopolymer, and the high-molecular-weight copolymers, **1(a + b)**, (**1 + 3**)**a**, and their reduced analogues, were obtained. Remarkably, the polymers with dibenzo-18-crown-6 ether units in the main chain contain complexed water even after reduction.

Thus, a variety of crown-containing polymers can be obtained easily by performing metal-free polyacylation and reduction reactions.

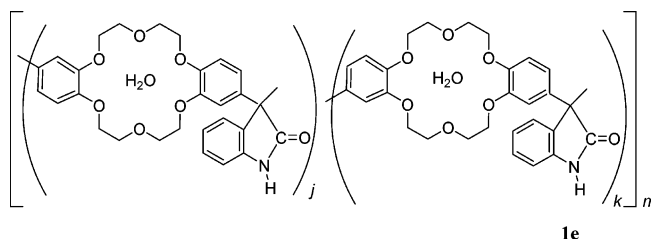
It was shown recently that in situ reaction of functionalized macrocycles containing acid groups with bisphenols may produce rotaxanes. Polymers obtained via melt condensation of bis(5-carboxy-*m*-phenylene)-32-crown-10-ether with bisphenol A by the Higashi method were found to give a polyrotaxane network, judging from the formation of insoluble, but swellable elastomeric material.¹⁰

Clearly, that dibenzo-18-crown-6-ether was too small to be threaded, even by a polymethylene chain, but reactions involving larger-size macrocycles **3** and **4** may, in principle, result in the polyrotaxanes. Thus, ¹H NMR spectra of the polymers **3b** and **4b** (Figure 3) reveal the presence of small signals in all aromatic, oxyethylene, and aliphatic fragments. (NMR spectra of the individual macrocycles, or acids, or their mixtures did not indicate any additional peaks).

However, analysis of polymers **3b** and **4b** by nuclear Overhauser effect spectroscopy (NOESY) did not reveal any through-space correlation between the protons of the macrocycle and the aliphatic spacer, e.g., intra-annular H and the methylene groups of acid residue, which would be expected for a threaded polymer. It is worthy to note that problems with threading detection by means NOESY were mentioned previously as well.¹⁰ Possibly, the extent of rotaxane formation is below the detection limit of the NOE experiment.

The properties of the polymers are presented below. As expected, relatively low softening temperatures (T_{soft}) (which may be referred to as apparent T_g) are found for polymers with long aliphatic spacers. Therefore, development of crown-ether-based polymers as catalysts or catalyst supports will require polymers with T_{soft} well above of the reaction temperature. To address this problem, we also investigated the condensations of crown ethers with isatin. Recently, we reported that isatin reacts with aromatic hydrocarbons under superacid conditions to give poly(arylene oxyindole)s.¹¹ It turned out that the condensations of isatin with macrocycles **1–4** in Eaton reagent proceed readily at room temperature, affording high-molecular-weight polymers for 1.5–2 h.

As with the polymers from crown ethers and diacids, NMR studies also revealed the presence of two isomer structures. Thus, the chemical composition of, for example, polymer **1e**, obtained by condensation of crown ether with isatin, can be presented by the following formula: Condensations of isatin

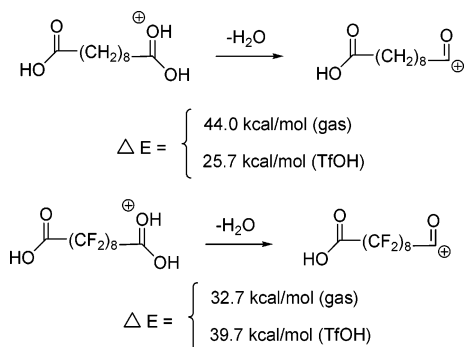


(or its mixture with diacids) with crown ethers or with a mixtures of crown ethers also afforded high-molecular-weight polymers.

3.2. Mechanistic Aspects. **3.2.1. Polyacylation.** Although aromatic electrophilic substitution reactions catalyzed by Eaton's reagent or polyphosphoric acid are widely employed in organic and polymer chemistry, the reaction mechanisms are incompletely understood. The reactions are believed to be of the Friedel–Crafts type, but the actual attacking electrophiles are not known with certainty. Eaton ruled out methanesulfonic acid (MSA) and its anhydride as the catalytic species and speculated that the true catalyst was a mixed MSA–P₂O₅ anhydride.¹² Methanesulfonic anhydride and the mixed anhydride from MSA and phosphoric acid are present in Eaton catalysts.¹³ Because both polyphosphoric acids and MSA–P₂O₅ are effective catalysts, whereas MSA/methanesulfonic anhydride (MSAH) is not, it follows that the acylating agent is a phosphoric carboxylic mixed anhydride. Because alkylsulfonates are better leaving groups than phosphates or phosphonates in carbocationic solvolyses, and high reactivity of mixed carboxylic methanesulfonic anhydrides in acylation reactions was unambiguously demonstrated,¹⁴ the inability of MSA/MSAH mixtures to catalyze acylations by carboxylic acids must be due to the slow rate of formation of the mixed anhydride.

The above-described reactions of dibenzo-crown ethers with sebacic, 1,12-dodecanedicarboxylic, 1,16-hexadecanedioic, and 1,4-phenylenediacetic acid in an Eaton's reagent medium gave high-molecular-weight polymers. Similarly, condensations involving dibenzo-crown ethers and 1,3- and 1,4-cyclohexanedicarboxylic acids also afforded film-forming polymers. However, reactions of dibenzo-crown ethers with aromatic dicarboxylic acids, e.g., terephthalic and isophthalic, produced only low-molecular-weight products. The low reactivity of aromatic dicarboxylic acids is attributed to "resonance stabilization of the resulting acylium ion."⁵

To clarify the influence on the reaction of groups adjacent to carbonyl groups, we condensed dibenzo-crown ethers with perfluorosebacic acid (PFSA), which exhibited sharply lowered reactivity. Condensations of dibenzo-crown ethers with PFSA in pure trifluoromethanesulfonic acid (TfOH) also failed. To explain the low reactivity of PFSA, we carried out theoretical calculations. Because the active species in the reaction of electrophilic substitution is a carbocation, we estimated the energies of dissociation of protonated acids (sebacic and perfluorosebacic) to give the respective carbocations and water molecules. The gas-phase dissociation energies of protonated sebacic and perfluorosebacic acids to form carbocations are 44.0 and 32.7 kcal/mol, respectively; this can be explained by carbocation stabilization by participation of lone pairs of fluorine atoms. However, when solvation is taken into account, the dissociation of protonated sebacic acid is more favorable compared with that of PFSA (25.7 and 39.7 kcal/mol, respectively) because of better solvation of the sebacic carbocation.

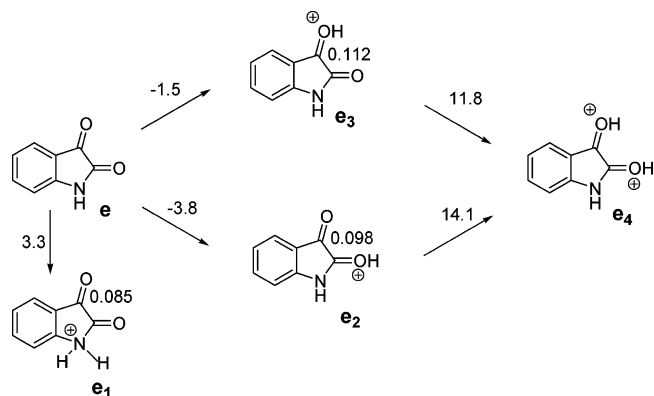


In principle, carbocation stabilization could be due to the contribution of C–F σ -bond electrons (similar to C–H bond hyperconjugation). However, if the stabilization of carbocations by σ electrons of C–F bonds occurred, the same stabilization would be observed in nonfluorinated acids because of σ electrons of C–H bonds (they have the same symmetry). Calculations show that this is not the case. According to natural population analysis of carbocations, the natural charges of sebacic and perfluorosebacic cations are +0.96 and +0.86, respectively, which shows clear stabilization of positive charges in the latter case. The origin of this stabilization may be understood by comparing the occupation of 2p orbitals of fluorine atoms adjacent to a carbocationic center with those in the middle of a perfluorinated chain. Thus, for the first case (2 fluorine atoms), the 2p level has 5.43 electrons, whereas in the latter, the 2p level shows occupation from 5.48 to 5.51 electrons. This allows estimation of the contributions of 2p electrons of F atoms to the stabilization of a carbocationic center. As seen, the whole electron density build up of 0.1 electron can be attributed to the participation of 2p electrons of fluorine atoms adjacent to a carbocation center. Therefore, the reactivity of sebacic acid is controlled mainly by solvation of a carbocation and not the electronic influence of substituents. (In this case, we neglected anhydride formation because the reaction was carried out in pure TfOH).

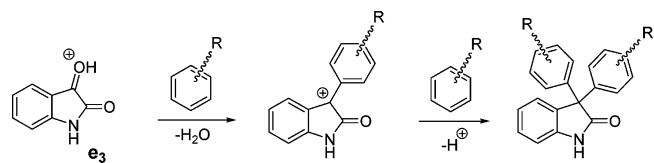
3.2.2. Polyhydroxyalkylation. The acid-catalyzed condensation of aldehydes, ketones, and α -diketones with aromatic hydrocarbons, called hydroxyalkylation, is also considered to be a Friedel–Crafts-type reaction. Recent progress in the chemistry of electrophilic intermediates, especially by G. A. Olah, led to superelectrophilic hydroxylation reactions in which carboxonium intermediates react with Lewis or Brønsted acids to give extremely reactive dications.¹⁵

Diprotinated species are known to be responsible¹⁵ for the unusually high reactivity of carbonyl-containing molecules toward some aromatic hydrocarbons. Therefore, it seems that diprotinated carbonyl or dicarbonyl species are important for the reactions under consideration.

To establish the nature of the reactive species, reactions of isatin with aromatic mono- and diprotinated isatin intermediates were studied theoretically. Calculations showed that, even in TfOH solution, diprotonation is difficult. Thus, the reaction energy between isatin and two molecules of TfOH to produce the most stable diprotinated intermediate **e**₄ requires 14.1 kcal/mol, starting from the most stable monoprotonated species **e**₂, where the amide carbonyl is protonated. As shown in the following scheme, the most abundant species in TfOH solution must be **e**₃ and **e**₄, with a difference in stability between them of 2.3 kcal/mol.



To estimate the most reactive intermediate, local electrophilic Fukui functions (f^+) at ketone carbonyl carbons of intermediates **e**₁–**e**₃ were calculated as follows: $f^+ = q(N+1) - q(N)$, where $q(N)$ is the Mulliken charge at a given carbon atom of a studied molecule and $q(N+1)$ is the Mulliken charge at the same atom with an extra electron.¹⁶ As shown, the carbonyl carbon is the most electrophilic in structure **e**₃. On the other hand, the *N*-protonated molecule **e**₁ is the less stable and less reactive. Therefore, the probable reactive intermediate is **e**₃ when the reaction is under kinetic control, and the reaction involving isatin can be presented as follows: However, we cannot completely



discard participation of the most stable intermediate **e**₂ because the difference in f^+ between two molecules is small.

3.3. Polymer Properties. The polymers obtained in this work are fully soluble in chlorinated (except the polymers containing isatin residue) and aprotic solvents or strong acids, but insoluble in alcohols, aromatic hydrocarbons, or ethers. Transparent, strong, flexible films could be cast from the polymer solutions. Some properties of the polymers are presented in Table 1.

The methylene-bridged polymers in general have similar values of viscosity, but significantly lower melting points than their parent polyketones. Determination of T_g of the polymers by the DSC method turned out to be unexpectedly problematic (see below regarding the morphology of these polymers), and so we turned instead to thermomechanical analysis. Softening temperatures for the majority of the polymers range from 80 to 90 °C. Introduction of bulky side oxyindole groups essentially increases softening temperatures. Remarkably, DSC studies of the polymers obtained (except those containing dibenzo-21-crown-7 ethers) revealed the presence of strong endothermic transitions on heating (Figure 7), (for copolymers, even a few (Figure 8)). The second DSC scan of polymer **1a** reveals an exothermic peak around 120 °C, which can be attributed to the crystallization of a fraction of amorphous material that did not crystallize during cooling from the molten state after the first DSC scan. It is known that the first DSC scan of a polymer material is affected by the morphology and sample preparation conditions. Thus, the second DSC run would be free of the sample's history. Then, the main differences observed between the first and second scans of Figures 7–9 should be attributed to the sample morphology developed during sample preparation. Such sample morphology will be destroyed upon melting of

Table 1. Properties of the Polymers Synthesized

polymer code	crown ether	HOOC-R-COOH	polymer "as obtained"					reduced polymer				
			η_{inh}^a , (dL g ⁻¹), (TCE) ^a	M_w (g/mol)	M_n (g/mol)	T_{soft} (°C)	T_m (°C)	η_{inh}^a , (dL g ⁻¹), (TCE) ^a	M_w (g/mol)	M_n (g/mol)	T_{soft} (°C)	T_m (°C)
1a	18-6	-(CH ₂) ₈ -	0.93	64 020	29 100	94	162	1.05	66070	25 410	88	138
1b	18-6	-(CH ₂) ₁₂ -	1.46	84 400	46 890	89	162	1.30	83800	39 900	78	130
1c	18-6	-(CH ₂) ₁₄ -	0.65	40 100	21 100	88	152	0.72	39 800	21 170	73	123
1d	18-6	-CH ₂ -Ph-CH ₂ -	1.11	69 040	30 020	118	144	1.02	67 300	33 680	83	180
1(a + b)	18-6	-(CH ₂) ₈ -/- (CH ₂) ₁₂ - (50/50)	1.14	58 710	20 960	95	110 140	1.05	57 090	21 010	90	115
1e	18-6	isatin	1.20 ^b	62 400	32 840	217						
2b	21-7	-(CH ₂) ₁₂	0.98	73 200	17 830	80		1.04	74 030	21 150	75	
3a	24-8	-(CH ₂) ₈ -	0.82	59 360	24 730	82	100	0.78	57 550	23 980	63	75
3b	24-8	-(CH ₂) ₁₂	0.94	60 830	21 720	75	99	0.80	58 910	18 410	60	70
(1 + 3)a	18-6/24-8	-(CH ₂) ₈ -	0.88	53 410	29 670	90	115	0.86	52 230	26 240	80	
3e	24-8	isatin	0.88 ^b	47 300	21 500	144						
4b	30-10	-(CH ₂) ₁₂ -	0.67	37 200	14 370	63	78	0.62	35 280	13 070	60	70

^a TCE: *sym*-1,1,2,2-tetrachloroethane. ^b Measured in NMP.

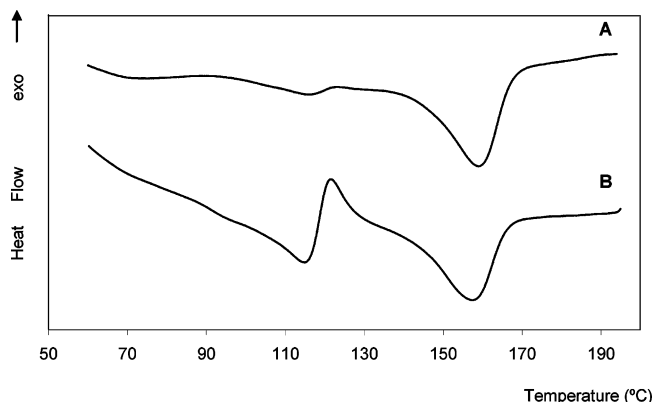


Figure 7. DSC traces of polymer **1a**. (A): First scan. (B): Second scan.

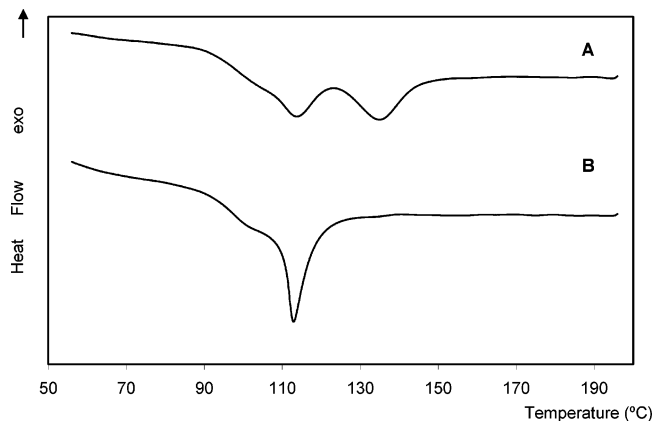


Figure 8. DSC traces of copolymer **1(a+b)**. (A): First scan. (B): Second scan.

the sample, and it is not developed again during a consecutive DSC run of the sample. This is particularly evident in the case shown in Figure 8, where the second endothermic peak is missing in the second scan. It is also significant that reduction of polymer **1d** (which displays only a very weak endotherm on the first scan and no transitions during the second one) produces a polymer capable of cold crystallization from the glassy state followed by an intense endothermic process at higher temperature (Figure 9).

Scanning electron microscopy of polymer **1d**, crystallized from the melt, shows globular structure (Figure 10.) Higher magnification reveals the presence of small elongated fibrils (Figure 10, bottom).

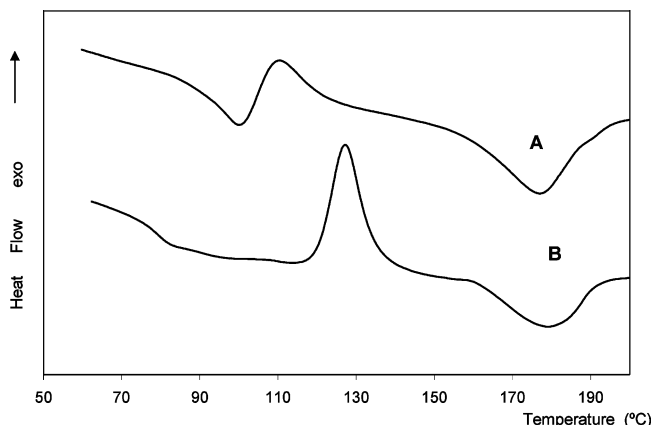


Figure 9. DSC traces of polymer **1dH**. (A): First scan. (B): Second scan.

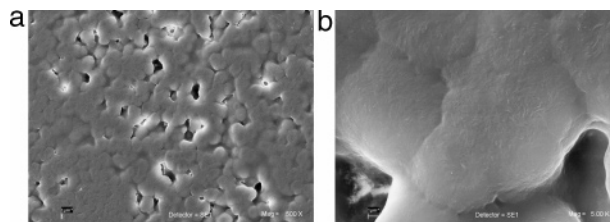


Figure 10. SEM pictures of polymer **1dH**.

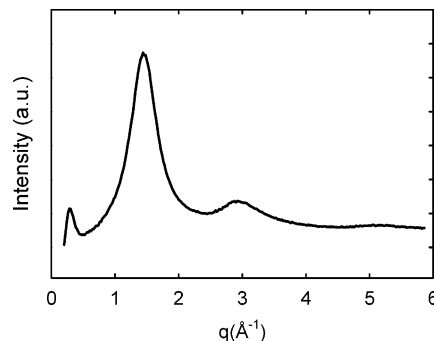


Figure 11. X-ray intensity as a function of q for the solution cast film of polymer **1a**.

The DSC data at first sight suggest that the reduced polymers are semicrystalline, though this would be very surprising, taking into account the presence of equal proportions of syn- and anti-substituted crown ether residues in the main chain.

Figure 11 illustrates the X-ray diffractogram, at room temperature, typical of the series of polymers described above.

It shows two broad wide angle peaks ($q \sim 1.5$ and 3.0 \AA^{-1}) and a sharper reflection located in the medium angle region ($0.2 \text{ \AA}^{-1} < q < 0.5 \text{ \AA}^{-1}$). The specific value of q for this medium-angle reflection is a function of both the length of the alkyl sequence and the size of the crown ether. The occurrence of a strong, sharp reflection at medium angle, together with the broad peaks in the wide angle region, may be an indication that the observed order in such systems reflects a frozen smectic-A or smectic-C phase, in which the crown ether groups align to form a rather perfect layer structure but with low lateral order, rather than full, three-dimensional crystalline morphology. Formation of mesophases in these polymers is in agreement with known data on the self-assembly of a two-armed polymer with a crown ether core¹⁷ and with previous work on liquid crystalline polymers and small molecules containing dibenzo-crown ethers.¹⁸ A possible mechanism of self-assembly depends on the known affinity between dibenzo-crown ether cores, but a more detailed study of this novel polymer morphology is now in progress and will be reported elsewhere.

Because crown-ether–water complex formation in a polymer could modify the binding properties of the crown ether fragment, we studied the complexation of model 3,4'-diacetyl-dibenzo-18-crown with potassium ion in the presence of water molecules.

By following the methodology adopted for studying of a crown-ether–water complex, first, conformational search of a system crown-potassium-ion–water molecule using the MMFF force field was carried out to locate the lowest energy conformer, followed by B3LYP/6-31 G* geometry optimization of the located structure. The calculated binding energy of crown-ether–water complex is just -2.9 kcal/mol , while the experimental binding energy of dibenzo-18-crown-6–potassium ion complex is $-52.8 \pm 4.5 \text{ kcal/mol}$ (comparing reasonably well with calculated binding energy at B3LYP/6-31 G* level (-46.8 kcal/mol)).¹⁹

As seen, the formation of a crown-ether–water complex barely affects the complexation capability of crown ring toward metal ions.

4. Conclusions

In summary, we have demonstrated for the first time a simple and reliable preparation of film-forming polymers and copolymers containing main-chain dibenzo-18-crown-6, dibenzo-21-crown-7, and especially, dibenzo-24-crown-8 and dibenzo-30-crown-10 ether units alternating with aliphatic (C_{10} – C_{16}), aliphatic–aromatic spacers, or oxyindole fragments. Structural studies revealed the presence of two isomeric structures (syn- and anti-substituted crown ether residues) within the polymer chains. It should be noted that satisfactory results were obtained, even by students with no special training.

The polymers with “symmetrical” crown ether units, such as dibenzo-18-crown-6, dibenzo-24-crown-8, or dibenzo-30-crown-10 ethers, display strong melting endotherms, which seem to arise from ordered (possibly smectic) layer structures formed by correlated stacking of the dibenzo-crown ether units. Even random copolymers, especially those containing different crown ethers, can show endothermic transitions (and thus supramolecular organization).

The polymers synthesized are convenient materials for the investigations of the effects of minor and progressive changes in size, organophilicity, and electron-donating and -withdrawing capacity of crown ethers on their performance as neutral ionophores in phase-transfer catalysis and membrane transport of ionic substance, the effect of the polymer matrix on the properties of crown-ether-containing polymers. The phenomenon of complexation between polymeric dibenzo-18-crown-6 and

water allows for fine-tuning of the properties of the materials. Besides, the polymers and their derivatives are of obvious interest for construction of different supramolecular assemblies, including, potentially, molecular machines.

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References and Notes

- (1) (a) Luttringhaus, *Ann. Chim.* **1937**, 528, 181–210. (b) Luttringhaus, *Ann. Chim.* **1937**, 528, 211–222. (c) Luttringhaus, *Ann. Chim.* **1937**, 528, 223–233.
- (2) (a) Pedersen, C. J. *Am. Chem. Soc.* **1967**, 89, 7017–7036. (b) Pedersen, C. J. In *Synthetic Multidentate Macrocyclic Compounds*; Izatt, R. M., Christensen, J. J., Eds.; Academic Press: New York, 1978.
- (3) (a) Laidler, D. A.; Stoddart, J. F. *The Chemistry of Ethers, Crown Ethers, Hydroxy Groups, and their Sulfur Analogues*, Supp. E, Part 1, John Wiley: New York, 1980; Supplement E, Part 1. (b) Vogtle, F.; Weber, E., Eds.; *Host–Guest Complex Chemistry of Macrocycles: Synthesis, Structure, Applications*; Springer-Verlag: Berlin, 1985. (c) Gokel, G. *Crown Ethers and Cryptands*; Royal Society of Chemistry: London, 1991. (d) Krakowiak, K. E.; Bradshaw, J. S.; Zamecka-Krakowiak, D. J. *Chem. Rev.* **1989**, 89, 929–942. (e) Dietrich, B.; Viout, P.; Lehn, J.-M. *Macrocyclic Chemistry: Aspects of Organic and Inorganic Supramolecular Chemistry*; VCH: Weinheim, 1993. (f) Gong, C. G.; Gibson, H. W. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 2331–2333. (g) Mahan, E.; Gibson, H. W. In *Large Ring Molecules*, 2nd ed.; Semlyen, J. A., Ed.; Kluwer: Dordrecht, 2000; pp 415–560. (h) Gong, C.; Gibson, H. W. In *Molecular Catenanes, Rotaxanes, and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C. O., Eds.; Wiley-VCH: Weinheim, 1999; pp 277–321. (i) Gokel, G. W.; Leevy, W. M.; Weber, M. E. *Chem. Rev.* **2004**, 104, 2723–2750.
- (4) (a) Tunca, U.; Yagci, Y. *Prog. Polym. Sci.* **1994**, 19, 233–286. (b) Fabre, B. Simonet, J. *Coord. Chem. Rev.* **1998**, 178–180 (2), 1211–1250. (c) Cowie, J. M. G. *Polym. Int.* **1998**, 47, 20–27. (d) Spiro, D.; Alexandratos, S. D.; Stine, C. L. *React. Funct. Polym.* **2004**, 60, 3–16.
- (5) Ueda, M.; Kano, T.; Warragai, T. *Makromol. Chem., Rapid Commun.* **1985**, 6, 847–850.
- (6) (a) Newkome, G. R.; Taylor, H. C. R.; Fronczek, F. R.; Delord, T. J.; Cooli, D. K. *J. Am. Chem. Soc.* **1981**, 103, 7376–7378. (b) Bryan, S. A.; Willis, R. R.; Moyer, B. A. *J. Phys. Chem.* **1990**, 94, 5230–5233. (c) El-Eswed, B. I.; Zughil, M. B.; Derwish, G. A. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1997**, 28, 245–248. (d) Fromm, K. M.; Gueneau, E. D.; Goesman, H.; Bochet, C. Z. *Anorg. Allg. Chem.* **2003**, 629, 597–600.
- (7) Stott, P. E.; Bradshaw, J. S.; Parish, W.; Copper, J. W. *J. Org. Chem.* **1980**, 45, 4716–4720.
- (8) (a) Kursanov, D. N.; Parnes, Z. N.; Basova, G. I.; Loim, N. M.; Zdanovich, V. I. *Tetrahedron* **1967**, 2235–2238. (b) West, C. T.; Donnelly, S. J.; Kooistra, D. A.; Doyle, M. P. *J. Org. Chem.*, **1973**, 38, 2675–2681.
- (9) Ben-Haida, A.; Colquhoun, H. M.; Hodge, P.; Lewis, D. F. *Polymer* **1999**, 40, 5173–5182.
- (10) Gibson, H. W.; Nagvekar, D. S.; Powell, J.; Gong, C.; Bryant, W. S. *Tetrahedron* **1997**, 53, 15197–15207.
- (11) Colquhoun, H. M.; Zolotukhin, M. G.; Khalilov, L. M.; Dzhemilev, U. M. *Macromolecules* **2001**, 34, 1122–1124.
- (12) Eaton, P. E.; Carlson, C. R.; Lee, J. T. *J. Org. Chem.* **1973**, 38, 4071–4073.
- (13) Farcasiu, D.; Cao, H. *J. Mol. Catal.* **1994**, 87, 215–222.
- (14) (a) Effenberger, F. *Angew. Chem.* **1980**, 19, 151–230. (b) Effenberger, F.; Epple, G.; Eberhard, J. K.; Buhler, U.; Sohn, E. *Chem. Ber.* **1983**, 116, 1183–1194.
- (15) Olah, G. A. *Angew. Chem.* **1993**, 32, 767–922.
- (16) Yang, W.; Mortier, W. J. *Am. Chem. Soc.* **1986**, 108, 5708–5711.
- (17) Fu, J.; Cong, Y.; Yu, X.; Pan, C.; Yang, Y.; Lia, B.; Han, Y. *Polymer* **2004**, 45, 7389–7394.
- (18) (a) Fischer H.; Zuev, V. V. *Polym. Bull.* **1994**, 32, 559–563. (b) Fischer, H.; Karasz, F. E. *Acta Polym.* **1994**, 45, 308–311. (c) Lipatov, Yu. S.; Tsukruk, V. V.; Shilov, V. V.; Pastushok, V. N.; Galatina, A. I.; Bogatskii, A. V. *Dokl. Akad. Nauk SSSR*, **1985**, 285, 155–158. (d) Percec, V.; Turkaly, P. J.; Asandei, A. D. *Macromolecules* **1997**, 30, 943–952.
- (19) Anderson, J. D.; Paulsen, E. S.; Dearden, D. *Int. J. Mass Spectrom.* **2003**, 227, 63–76.